

CHARACTERIZATION OF UNSUPPORTED MoS_2 CATALYSTS BY CONTROLLED-
ATMOSPHERE PROGRAMMED-TEMPERATURE OXIDATION

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INTRODUCTION

Controlled-atmosphere programmed-temperature oxidation, CAPTO, has been used as an effective tool for the quantitative determination and characterization of carbon, hydrogen, and sulfur in coal¹ and related materials.² This technique now has been applied here to provide unique, new information on the oxidation reactivity of sulfur in a variety of unsupported MoS_2 catalysts and of the carbonaceous deposits sometimes associated with them. In this application, the CAPTO analysis provides quantitative determination of three of the key elements in the structure of the working catalysts: sulfur, carbon, and hydrogen. Further, interpretation of the temperature profiles for the evolution of the oxides of these elements provides valuable information on the chemical state of these elements in the particular catalyst under study. This combination of information can shed more light on the structural differences among catalysts prepared by different methods and on the changes that may result from exposure to the processing conditions found under typical hydrotreating applications. To assess the potential of this analytical technique, a series of dispersed catalysts prepared by a variety of widely different methods was analyzed by CAPTO. The results indicate that the method is a useful, new means to characterize these materials.

Molybdenum disulfide has been used for a long time as the basis for many unsupported catalysts used for hydrotreating and related processing applications including direct coal liquefaction.³ Unsupported catalysts of this type have been prepared by various methods using any one of several molybdenum compounds as precursors. Promoted MoS_2 catalysts have been prepared by introducing minor amounts of other metals, primarily cobalt, nickel, or iron. In many cases, the catalyst is prepared *in situ* by the addition of a catalyst precursor just prior to the introduction of the feedstock to the hydrotreating reactor. Typically, this mode of preparation leads to a catalytic material that contains MoS_2 in close contact with a carbonaceous deposit.⁴ Alternatively, the MoS_2 may be generated separately and introduced to the reactor as a pure compound. Both approaches have been used in this work to generate a small set of catalysts of different crystallite sizes and with different degrees of crystallinity. In particular, the exfoliation and restacking technique^{5,6,7,8} has proven to be very valuable as a means to manipulate the structure of MoS_2 . Analysis of these materials by CAPTO provided "fingerprints" of the susceptibility of the sulfur in these catalysts to oxidation. Comparison of the different fingerprints from each sample indicated that the relative prominence of characteristic peaks may be related to the individual history of the catalyst's preparation and use.

EXPERIMENTAL

The CAPTO apparatus has been described previously.¹ Briefly, the sample is mixed with an inert diluent, WO_3 , and packed in a quartz tube. The device heats the sample according to a programmed temperature ramp, typically 3°C min^{-1} . In these analyses, a stream of 100% oxygen was passed through the sample plug. The gas flow was regulated by a mass flow controller. Complete combustion of the gases from the primary reactor was obtained by passage through a secondary catalytic reactor held at 1050°C . An FTIR was used to monitor the exit stream for CO_2 , SO_2 , and H_2O . The detector response was calibrated, allowing the final output to be plotted in terms of the mass of each element evolved as a function of sample temperature. Integration of the area under the curves provided the total mass of each element evolved from a sample, and thus the elemental analysis for carbon, hydrogen, and sulfur. Information

about the chemical forms in which these elements exist in the sample was available from the recorded temperature profiles. The total envelope for each gas was resolved by a peak fitting program into a set of individual peaks, each centered about a characteristic temperature. Experience obtained from the analyses of a wide variety of coals and well-characterized reference materials has made possible the association of the various characteristic temperatures with different chemical forms of the elements. For example, aromatic carbon is readily distinguished from other forms of carbon, and may be quantitatively determined.

CAPTO analysis was carried out on a series of fresh and used catalysts prepared by different methods. Exfoliation techniques were used as one means to manipulate the physical and chemical properties of MoS_2 catalysts. This method has been used to disassemble highly crystalline MoS_2 to form single layers suspended in water, followed by restacking of the layers to regenerate MoS_2 in a less-ordered crystalline form. The experimental procedures used here have been reported in a study of the application of this technique to generate MoS_2 catalysts for use in coal liquefaction and petroleum resid upgrading.^{7,8}

The exfoliated/restacked catalysts used here were prepared by first intercalating a commercial sample of MoS_2 (Alpha) with Li by reduction with 2.5 M n-butyllithium in hexanes (Aldrich) for two or three days in a glove box. The intercalated solid was filtered, dried, then removed from the glove box and added to water agitated by an ultrasonic bath. On addition to water, a suspension developed which is typically associated with the formation of single layer MoS_2 . The suspension settled on standing as the restacking of MoS_2 proceeded. The restacked material was filtered, washed, and dried under vacuum.

An *in situ* preparation method was used as another route to MoS_2 . A mixture of 4 g dodecane, 2 g pyrene, 0.3 g sulfur, and 0.5 g ammonium molybdate (2.43 mmole Mo) dissolved in 3 g water was added to a 40 mL high-pressure microautoclave. The vessel was pressurized with 500 psig hydrogen, heated to 380 °C over the course of about 1 h, then held at this temperature for another 1 h. Agitation was provided by shaking the reactor. After cooling, the catalyst was recovered by filtration, washed with tetrahydrofuran, and dried under vacuum.

An example of a used catalyst was obtained by recovering it after a standard test for hydrotreating activity.⁸ A mixture of 0.32 g exfoliated/restacked MoS_2 , 3.23 g tetralin, and 3.0 g Hondo resid was added to a 40 mL microautoclave. The reactor was charged with 1000 psig hydrogen and heated over the course of about 1 h to 425 °C, then held at this temperature for another 1 h. The reactor was quenched in water, and the product analyzed by determination of heptane solubility using a pressure filtration method. The catalyst was recovered by washing the heptane insoluble portion with tetrahydrofuran, again using the pressure filtration method. The recovered catalyst was dried in a vacuum oven.

The catalysts were also examined by other methods to obtain comparative data, including SEM, X-ray diffraction, BET surface areas, and elemental analyses.

RESULTS AND DISCUSSION

Sulfur Profiles. The same highly crystalline sample of MoS_2 used as the starting material for the exfoliation/restacking method of catalyst preparation was analyzed by CAPTO to provide a reference. The sulfur profile is shown in Fig. 1A. SO_2 evolved producing a broad envelope of peaks beginning about 220 °C and ending by 580 °C. The shape of the whole complex envelope was well simulated by a combination of four peaks. The central temperature and relative area associated with each peak is given in Table 1. The majority of sulfur in this sample lies under the peak at highest temperature, centered around 507 °C. The general appearance and wide breadth of the total sulfur profile reflects considerable variability in sulfur oxidation reactivity. The separation of the total envelope into a series of separate peaks gives evidence that the sulfur contained in the single compound, MoS_2 , may be consist of several distinct populations, each associated with a characteristic oxidation temperature.

The sulfur profile for the exfoliated/restacked sample of MoS_2 is given in Fig. 1B. The considerable change in physical structure induced by this treatment is reflected by a profoundly different sulfur profile. The broad envelope of this new profile begins at about 220 °C, just as it does with the highly crystalline starting material. However, the majority of sulfur dioxide from the restacked material evolves at comparatively lower temperatures and the profile already returns to baseline by about 500 °C rather than 580 °C. That means the major oxidative event was complete before

reaching the temperature of the maximum rate of SO_2 evolution observed for the highly crystalline starting material. The large envelope was again very broad and could be resolved into four individual peaks. The pronounced shift to lower oxidation temperatures after exfoliation/restacking implies that the degree of crystallinity of the catalyst is a major factor governing the reactivity of sulfur in MoS_2 toward oxidation. In addition, a small isolated peak centered at 628°C now also appears. Peaks in this area are often associated with metal sulfates.

A third sample was investigated to determine the effect of exposure to hydrotreating conditions on the exfoliated/restacked catalyst. An exfoliated/restacked catalyst sample prepared in the same way as described above was used in hydrotreating Hondo resid⁸ under the conditions summarized in the experimental section. The sulfur profile is given in Fig. 1C. Compared to the fresh catalyst, the center of gravity of the major peak has moved to a higher temperature. However, the endpoint of the major peak still comes at about 500°C , just as with the fresh exfoliated/restacked catalyst. The major envelope of the used catalyst could be resolved using three peaks rather than the four required for fresh catalyst. The three peaks of the used catalyst correspond rather well with three peaks of the fresh catalyst in terms of temperature and width. Comparison of the areas under the peaks reveals that the exposure to hydrotreating conditions for even only a single activity test made the recovered catalyst somewhat more resistant to oxidation. It should be noted that the CAPTO analysis for carbon demonstrated negligible amounts of coke were deposited on this sample. The possibility that sulfur in coke laid down by the Hondo resid contributed to the CAPTO profile for sulfur may be dismissed in this case.

The sulfur evolution profile of the catalyst prepared from ammonium molybdate by the *in situ* method was also obtained (not shown) for comparison to the previous samples. In contrast to both the highly crystalline and the exfoliated/restacked catalysts, the sulfur evolution profile for the MoS_2 catalyst derived from ammonium molybdate is dominated by a low temperature envelope. Again, individual peaks were resolved, five in this case. A difference was found in the atypical breadth of the peak centered at 429°C , which extensively overlapped two neighboring major peaks with widths more typical of the narrow peaks seen in the analyses of other samples of MoS_2 . These four CAPTO analyses demonstrate that there is a wide variation in the reactivity of sulfur in MoS_2 toward oxidation. Furthermore, the fingerprint characteristics obtained by CAPTO are related to the method of catalyst preparation and its history under processing conditions.

Table 1 contains the temperature and the relative amount of sulfur evolved for each peak for all four samples. When the resolved peaks are arranged in this way, it is apparent that there are corresponding peaks among the samples that have similar temperatures for peak maxima and generally similar widths. The CAPTO analyses give evidence that differences in the physical structure of MoS_2 are associated with differences in the distribution of sulfur among several characteristic types. Correlation with X-ray diffraction data, discussed below, shows that the relative amount of sulfur under peaks at higher oxidation temperatures increases with the degree of crystallinity.

Profound differences in crystallinity among the four MoS_2 catalysts became readily evident on comparison of their X-ray diffraction patterns. The highly ordered, three-dimensional structure of the original MoS_2 was apparent from the narrow peaks that compose the diffraction pattern. The 002 line was particularly prominent and narrow. The diffractogram of the exfoliated/restacked material was markedly different. Its broad lines were consistent with a turbostratic structure, indicating that order along the dimension of the stacking plane had been lost. The width of the 002 line at half-height was used to estimate the stacking heights of the crystallites for each sample. The changes in line width indicated that the exfoliation/restacking process reduced the average stacking height from 325 \AA to 185 \AA . An increased degree of crystallinity (loss of turbostratic disorder) was observed for the exfoliated/restacked catalyst recovered after hydrotreatment. However, the changes were modest, and the stacking height remained essentially unchanged at 185 \AA . The catalyst prepared *in situ* presented yet another picture. The 002 peak was the broadest of the four samples, yielding an estimate for average stacking height of 27 \AA . The XRD data thus confirmed that this set of four catalysts exhibits a wide range of crystallinity. When the XRD results are compared with the distributions of sulfur among the various CAPTO peaks, it is evident that the MoS_2 samples of lesser crystallinity and composed of smaller crystallites also have a larger portion of more readily oxidized sulfur.

CONCLUSIONS

The CAPTO technique provides important information about dispersed molybdenum sulfide catalysts. First, the method provided useful basic information in the form of the quantitative determination of the elements sulfur, carbon, and hydrogen, although these data were not discussed here. More importantly, the various patterns for sulfur oxidation with temperature observed for dispersed catalysts prepared by different means and of different crystalline structure indicate the method is quite sensitive to physical characteristics of each catalyst sample. This technique offers the potential for following changes in catalyst structure throughout the course of its preparation and use. Detailed correlation of the shapes of the SO_2 evolution profiles with catalyst activity is not yet possible with the small set of samples investigated so far. However, higher activity has been observed for the exfoliated/restacked catalysts as opposed to the highly crystalline sample¹⁰. The catalyst prepared by the *in situ* method appears to be as active as the exfoliated/restacked example. In general, it appears that higher activity may be associated with a less ordered and more easily oxidized structure.

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DISCLAIMER

Reference in this work to any specific commercial product is to facilitate understanding and does not necessarily imply endorsement by the United States Department of Energy.

Table 1. Characteristic Temperatures of Sulfur Evolution for MoS_2 Catalysts.¹

DESCRIPTION	PEAK TEMPERATURES, °C					
	1	2	3	4	5	6
CRYSTALLINE MoS_2		301 (2.7)	384 (3.0)	440 (28.5)	507 (65.7)	
EXFOLIATED/ RESTACKED	244 (2.1)	299 (2.2)	371 (15.4)	417 (76.6)		628 (3.7)
RECOVERED AFTER HYDROTREATMENT		289 (9.1)	381 (2.0)	425 (86.3)		600 (2.6)
PREPARED IN-SITU FROM AmMo		272 (50.8)	382 (23.9)	429 (10.1) 456 (14.2)		575 (1.0)

1. Central temperature of peaks from curve-fit. Area per cent in parentheses.

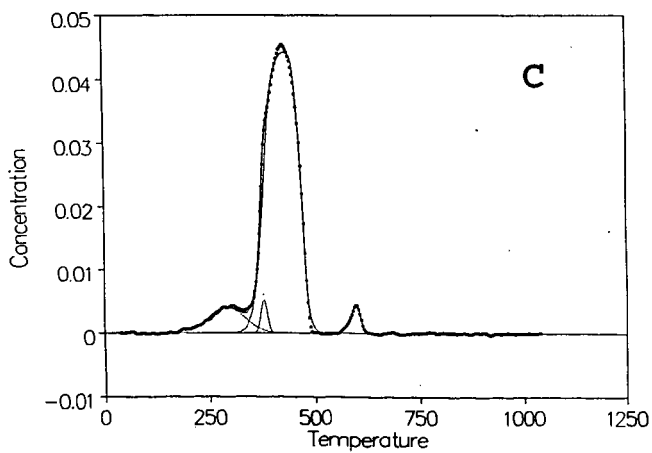
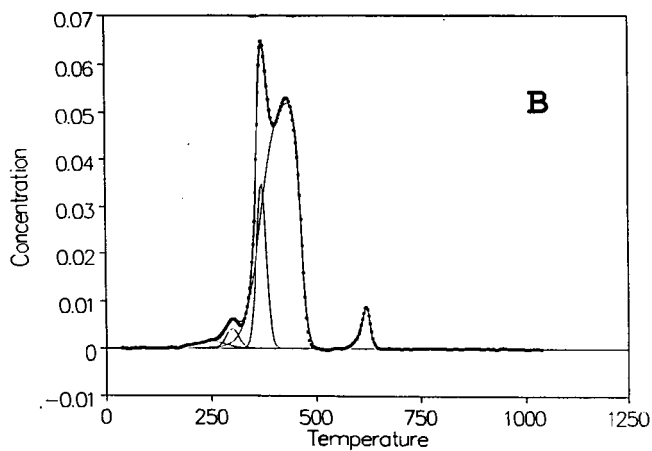
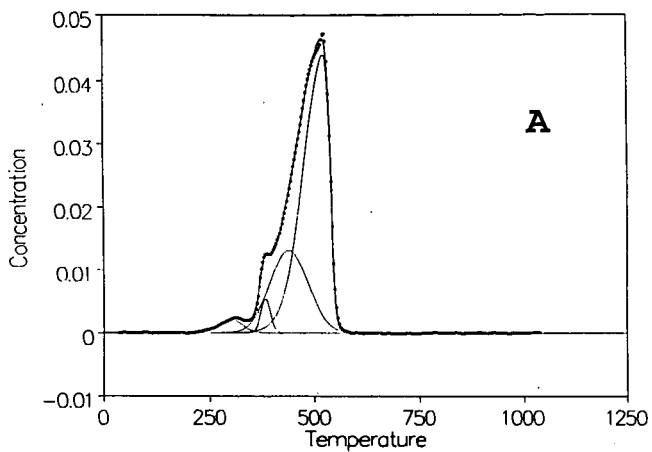


Fig. 1. CAPTO profiles of SO_2 evolution from MoS_2 . **A.** Crystalline MoS_2 . **B.** Exfoliated/restacked catalyst derived from sample A. **C.** Exfoliated/restacked catalyst recovered after use in hydrotreating Hondo resid.